Modelling Hydrogen-Metal Surface Interactions – The Integral Study

Anže Založnik, Iztok Čadež, Sabina Markelj
Jožef Stefan Institute
Jamova cesta 39
1000 Ljubljana, Slovenia
anke.zaloznik@ijs.si, iztok.cadez@ijs.si, sabina.markelj@ijs.si

Vida Žigman
University of Nova Gorica
Vipavska 13
5000 Nova Gorica, Slovenia
vida.zigman@ung.si

ABSTRACT

We present the numerical model for determining particle concentration in partially dissociated low pressure neutral hydrogen gas in a metal reaction cell where flowing gas is partially dissociated by a hot tungsten filament. Neutral hydrogen atoms and molecules in different vibrational states are taken into account. Available parameters for relevant surface processes (thermal dissociation, atom recombination, adsorption/desorption and vibrational relaxation) are used as initial input parameters. Calculated particle concentration distributions are compared to experimental data and qualitative agreement is obtained. Such a model is needed as a tool for in-depth understanding and interpretation of results from our specific experiment and thus in turn enabling checking and evaluating rates and cross sections for the above surface processes.

1 INTRODUCTION

Hydrogen interaction with surface of plasma wall and other plasma-facing components in tokamaks plays a crucial role in determining edge plasma characteristics, heat and particle load, modification of material property and fuel retention in the wall. This issue is especially important for controlling heat load to the divertor target plates by plasma detachment and to the total tritium retention. Modelling edge plasma as well as erosion and deposition of material requires detailed knowledge of reaction rates and cross sections for numerous relevant processes. More and more sophisticated modelling requires new processes to be included and their influence to be evaluated. Therefore, vibrational excitation and de-excitation of hydrogen molecules, dissociation from both ground and vibrationally excited states on hot surfaces and atom/ion recombination on metal surfaces are all significant for understanding and controlling the edge plasma characteristics. Rates and cross sections for these processes are needed especially for deuterium and tritium so that isotope effects are of high importance. We have been studying reactions involving neutral atoms and molecules experimentally by operating a hydrogen reaction cell as a source for vibrationally excited molecules in a low pressure regime (to ensure the dominance of particle-surface interactions) [1]. In order to enable interpretation and detailed analyses of experimental data we are developing physics-based modelling of the above listed interactions, taking into account the particular cell characteristics [2]. Alternatively, we also study H/D interaction with surfaces by the ion beam analytical methods [3].
The hydrogen reaction cell which is subject of the present modelling was described in more details in [1] and [2]. In short, this is a cylindrical metal cell in which a resistively heated tungsten filament is mounted. Wall of the cell is water cooled and temperature is monitored by a thermocouple. Hydrogen gas ($H_2$ or $D_2$) is introduced on the bottom side of the cell and after passing the cell it effuses through an orifice on the top base of the cell. Pressure in the cell is measured by a capacitive gauge and is kept low to ensure that the mean free path of molecules is much longer than the dimensions of the cell. Hydrogen molecules get dissociated at the hot filament which temperature is controlled by the heating current. Filament temperature dependence on heating current is determined separately by an optical pyrometer. As a result of a series of collisions with inner surfaces of the cell, dissociation on the filament, atom recombination on the wall and some inelastic collisions, hydrogen gas becomes a mixture of atoms and molecules in various vibrational states. The gas effusing through the exit orifice is crossed by an electron beam of a vibrational spectrometer which allows determination of the vibrational population distribution. This spectrometer employs specific properties of the dissociative electron attachment in hydrogen, [1] and [4].

The forward kinetic model presented in this paper includes $H_2$ molecules in all vibrational states (ground and 14 excited states), dissociated $H$ atoms and atoms adsorbed on the wall, and thus describes a system of 17 particle species in total, undergoing dominant particle-metal wall interactions. It represents an extension of a simplified initial model [2] and it is a continuation of our effort to provide a tool for analysis and interpretation of our previous experimental data. In order to "drive" the model, an initial dataset of state-specific transition probabilities for all above surface reactions are compiled using available theoretical and empirical data from literature. Tungsten, copper and stainless steel are of our main interest.

2 MODEL EQUATIONS

The present kinetic model describes the surface processes inside the reaction cell under low pressure conditions i.e. the influence of volume collisions can be neglected. Processes on the hot filament and on the cold cell wall are taken into account. On the hot filament we have considered sticking of molecules, followed by desorption of atoms as well as vibrationally excited molecules according to the Boltzmann distribution. On the cold walls we have taken into account de-excitation of vibrationally excited molecules, adsorption of hydrogen atoms, Eley-Rideal and Langmuir-Hinshelwood type recombination (e.g. [5]). Equations, describing the time evolution of particle densities due to all these processes, are:

$$
\frac{dn_j}{dt} = \frac{1}{4V} \sum_{i \neq j} n_i v_i (\alpha_{ij} S_h + \beta_{ij} S_c) - \frac{1}{4V} n_j v_j \sum_{i \neq j} (\alpha_{ji} S_h + \beta_{ji} S_c)
$$

$$
- \frac{1}{4V} n_j v_j \alpha_{at} S_h + \frac{1}{4V} n_{at} v_{at} n_{ad} S_c \sigma_{ER} P_{ER}^j - \frac{1}{4V} n_j v_j S_o
$$

$$
+ \frac{1}{V} k_{LH} S_c n_{ad}^2 \delta_{j0} + \frac{\eta}{V} \delta_{j0}
$$

(1a)

$$
\frac{dn_{at}}{dt} = \frac{1}{4V} \sum_i 2n_i v_i \alpha_{i, at} S_h - \frac{1}{4V} n_{at} v_{at} S_o - \frac{1}{4V} n_{at} v_{at} S_c S_{at}
$$

$$
- \frac{1}{4V} n_{at} v_{at} n_{ad} S_c \sigma_{ER}
$$

(1b)
Equation (1a) describes the time evolution of particle density $n_j$ for molecules in a particular vibrational state $j$ ($j = 0$ corresponds to the ground vibrational state). $n_{at}$ is the volume number density of free hydrogen atoms in the cell and $n_{ad}$ is the surface number density of atoms, adsorbed on cell walls. We take into account the molecules in ground and all 14 excited vibrational states. All sums run over $i = 0, \ldots, 14$. $V, S_c, S_h, S_o$ are geometrical parameters of the source cell - volume of the cell, surface of cold and hot areas and surface of the escape orifice, respectively. The pressure inside the cell is determined by the inflow of the gas, the conductivity of the source cell and the vacuum pumping speed.

Matrices $\alpha$ and $\beta$ are transition probability matrices, with elements $\alpha_{ij}$ and $\beta_{ij}$ denoting probabilities for molecule in $i$-th vibrational state to stick to filament surface and the wall, respectively and leave it in the $j$-th vibrationally excited state.

The first term of equation (1a) describes production of the $j$-th vibrational state on both, hot filament and cold wall, where $\frac{2n_{at}v}{\pi}$ is a number of collisions per unit time per unit area of molecules in $i$-th vibrational state. The second and the third term describe destruction of the $j$-th vibrational state by vibrational transition and dissociation on the hot filament, respectively. The fourth term is due to the Eley-Rideal recombination with cross section value $\sigma_{ER}$ in the $10^{-23} - 10^{-22}$ m$^2$ range \([3]\) and

$$P_{ER}^i = \frac{e^{-E_i/kT_v}}{\sum_j e^{-E_j/kT_v}} \quad (2)$$

the probability for formation of hydrogen molecule in $i$-th vibrational state, where $E_i$ is the energy of $i$-th vibrationally excited state. Experimental evidence indicates that vibrational states of molecules, formed by Eley-Rideal mechanism, are Boltzmann distributed with vibrational temperature $T_v$. Experimental values were found to be 2700 K and 3800 K for Cu and W surface, respectively \([1]\). Langmuir-Hinshelwood recombination is described by sixth term and only molecules in ground vibrational state are assumed to be formed. Here, $k_{LH} = \nu^{(2)} e^{-E_{des}/kT_w}$ is the rate coefficient for Langmuir-Hinshelwood mechanism with second order frequency factor $\nu^{(2)}$ in the $10^{-1} - 10^{-3}$ cm$^2$at$^{-1}$s$^{-1}$ range, the desorption energy $E_{des} \approx 1.6$ eV and the temperature of the cold wall $T_w$ (room temperature for present calculation) \([3]\). Fifth and the last term describe the escape of molecules from the exit orifice and inflow of hydrogen molecules in the ground vibrational state, respectively. The inflow of particles ($6.63 \cdot 10^{18}$ molecules/s for present calculations) is denoted by $\eta$.

Equation (1b) describes the time evolution of the number density of the free hydrogen atoms. Second and fourth term are similar to fifth and fourth term of the equation (1a), escaping of atoms from the cell and Eley-Rideal recombination, respectively. The first term describes the production of atoms by thermal dissociation on hot filament. The factor 2 is here because two atoms are obtained from every dissociated molecule. Adsorption of free atoms on the cold cell walls is described by the third term, where $st_c$ is the sticking parameter. According to \([5]\) the sticking parameter is calculated as

$$st_c = \frac{st_0}{1 + \Theta K} \quad (3)$$

where $st_0$ is the sticking probability at vanishing coverage $\Theta$. The coverage, $\Theta = \frac{n_{ad}}{n_{at}}$, is the ratio between the surface number density of adsorbed atoms and the density of adsorption sites on the
surface. The density of adsorption sites is taken to be \( n_{st} = 10^{19} \text{ m}^{-2} \). The constant \( K \) determines the shape of the \( s(\Theta) \) curve.

Model equation (1c) describes the time evolution of surface number density of atoms, adsorbed on the cold cell walls. First, second and third term describe adsorption of free atoms on the walls, Langmuir-Hinshelwood and Eley-Rideal mechanism, respectively.

As already mentioned, matrix elements \( \alpha_{ij} \) and \( \beta_{ij} \) describe the transition probability from \( i - th \) to \( j - th \) vibrational state on hot and cold surface, respectively. For calculation reasons we have added one column to both matrices and the elements of this column are dissociation probabilities. On the cold surface the dissociation is unlikely to occur thus the probabilities are taken to be 0. On the hot filament surface the probability for molecule dissociation is assumed to be independent of vibrational state of the molecule and is calculated so to reproduce experimental data from [6],

\[
P_{\text{diss}} = Ce^{-E_{\text{dis}}/kT_f},
\]

Here the pre-factor is taken to be \( C = 6300 \), \( E_{\text{dis}} = 2.19 \text{ eV} \) and \( T_f \) is the filament temperature. Elements \( \alpha_{i,at} \) for \( i = 0, \ldots, 14 \) are thus all equal to \( P_{\text{diss}} \). For calculation of all other matrix elements we have to calculate the probability for the molecule to desorb from the hot surface, \( P_{\text{des}} = s_{th} - P_{\text{diss}} \), where \( s_{th} \) is the sticking parameter on the hot surface i.e. the probability for the molecule to adsorb on the surface. Matrix element is then calculated as

\[
\alpha_{ij} = P_{\text{des}} e^{-E_j/kT_f} \sum_n e^{-E_n/kT_f}
\]

for \( i, j = 0, \ldots, 14 \) and the sum is running over all vibrational states. Desorbed molecules are assumed to obey Boltzmann distribution with vibrational temperature equal to the temperature of the hot filament \( T_f \) and the probabilities are assumed to be independent of the initial state of the molecule.

For the construction of \( \beta \) matrix, only de-excitations of the molecules on the cold cell walls are taken into account. The matrix is thus lower triangular and for the present calculations the elements are taken from [7].

Analogous calculations have already been performed [2] with the main difference that in the previous work the model equations were linear. Here we consider both Eley-Rideal and Langmuir-Hinshelwood type recombination separately, which brings about the non-linearity of equations (1) and thus the numerical methods differ. We also obtain additional non-linearity because of the dependency of the sticking parameter (3) on the number density of adsorbed atoms whereas it has been taken as a constant in previous work.

### 2.1 Numerical computation

First we have implemented the algorithm for solving the system of equations considering stationary condition. Left-hand sides of equations (1) were put to 0 and the modified version of Newton’s algorithm was used to find the roots of the functions. This algorithm requires the reduction of Euclidean norm of the residual on every step in order to improve the global convergence. If the step of an ordinary Newton’s method fails to reduce the norm then a reduced step in same direction is proposed.

We have also implemented a Runge-Kutta type algorithm to obtain the time evolution of number densities. It is a Prince-Dormand 9(8) method with adaptive step size. This method calculates the eighth- and ninth-order accurate solutions and the difference between them is taken to be the error of the solution. The stepsize control then uses this error estimate for the stepsize adaptation.
3 RESULTS

To test our model equations and numeric procedure we have performed a few sanity checks. One of them was to eliminate recombination and de-excitation on the wall and determine the vibrational temperature of the molecules in the cell. The vibrational temperature should be equal to the filament temperature since all vibrationally excited molecules are formed on the hot filament surface by assumed total thermal accommodation. Test program runs have confirmed such behaviour.

In our equations we have 9 parameters: inflow of the gas, sticking parameter on hot and cold surface, rate coefficient for Langmuir-Hinshelwood recombination, cross section for Eley-Rideal recombination, coefficient $K$ from equation (3), temperatures of hot filament and cold wall and vibrational temperature from equation (2). We want to understand how the solutions depend on all these parameters. In figure 1a we present the relative populations of all vibrational states for different filament temperatures for stationary condition and above described input parameters. Higher filament temperature results in higher dissociation probability and thus the number of free atoms in the cell is increased, as it is shown in figure 1b. The effect of Eley-Rideal recombination combined with wall relaxation is thus more pronounced and more vibrationally excited molecules are formed. For higher excitation energies populations are recombination/relaxation dominated and only intensity is dependent on filament temperature. We have fitted the obtained distributions of higher vibrational states, above 2.5 eV, by Boltzmann distribution, where the fitting parameter was vibrational temperature. For different filament temperatures these vibrational temperatures are approximately the same (parallel lines on semi log plot in figure 1a). They are about 50 K lower than the assumed $T_v = 3000$ K of molecules, produced by Eley-Rideal recombination.

![Figure 1: (a) Calculated relative populations of all vibrational states for filament temperature $T_f = 1600$ K, 1800 K and 2000 K. (b) Relative population of free atoms inside the cell as a function of filament temperature $T_f$.](image-url)
In another test we were varying the vibrational temperature $T_v$ of molecules produced by Eley-Rideal recombination, used in equation (2) and the results are shown in figure 2. In contrast to the case of varying the filament temperature, here only the population of higher vibrational states are changing with $T_v$. This result shows us that higher vibrational states depend highly on the Eley-Rideal recombination.

![Graph showing relative populations of vibrational states for different $T_v$.](image)

Figure 2: Calculated relative populations of all vibrational states for different $T_v$ of molecules produced by Eley-Rideal recombination - 2500 K, 3000 K and 3500 K; $T_f = 1600$ K.

## 4 CONCLUSIONS

The model for calculation of molecular and atomic concentrations and vibrational population distribution of molecules in hydrogen reaction cell taking into account basic surface processes on hot filament and cold wall is developed and tested. Results obtained with initial set of reaction parameters show all expected behavior and are in qualitative agreement with experimental results. This model is now going to be applied to our available experimental results and provide means for evaluation of parameters for included reactions. Its extension to other hydrogen isotopologues is straightforward. It will also help in planning and designing new experiments.

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## REFERENCES


